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A MODIFIED METHOD FOR DETERMINATION OF THE COPPER NUMBER OF PAPER

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A MODIFIED METHOD FOR DETERMINATION OF THE COPPER NUMBER OF PAPER

By B. W. Scribner and W. R. Brode

ABSTRACT

The copper number is a determination applied to paper to find its probable resistance to deterioration, and to control manufacturing processes so as to obtain satisfactory permanency. It is a measure of the amount of impure forms of cellulose which tend to weaken the paper and induce deterioration of the paper fiber.

Determination of the copper number of high-grade rag-fiber bond papers is difficult owing to the resistance these hard, tough papers offer to the usual procedure employed for this determination. A modified method is described by which greater accuracy in testing such papers was obtained and which is recommended in part at least for general usage in testing paper or pulp. It is patterned after the method of Gault and Mukerji and that of Staud and Gray. The variation from these methods considered of prime importance is grinding the test specimens to a finely divided condition. A grinder devised especially for the purpose is described in detail.

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I. INTRODUCTION

By the term, "copper number," as applied to the examination of celluloses is meant the amount of copper reduced from Fehling solution by a given amount of cellulose material. This determination,[1] commonly used in the examination of celluloses to find their content of oxidation products and other degraded celluloses, such modified celluloses having abnormally high copper values, is applied

[1] Originally proposed by Schwalbe, Die Chemie der Cellulose, p. 625; 1912.

to paper to find its probable resistance to chemical deterioration, as the oxycelluloses and other modified celluloses are less permanent than pure cellulose and tend to induce deterioration of the paper fiber. Such determination is also of assistance in controlling paper-making processes so as to minimize the effect of them in respect to chemical degradation of the cellulose of the fibrous raw material.

When the cellulose material is treated with Fehling solution, the copper sulphate of the latter is quantitatively reduced by the degraded celluloses to cuprous oxide. The amount of cuprous oxide so produced is conveniently measured by first using it to reduce a molybdophosphoric solution. The amount of reduced molybdenum solution is then determined by oxidizing it with potassium permanganate. The molybdate titration method is preferred as the color imparted by the molybdenum provides an excellent end point, both in the titration itself and in the washing of the precipitated cuprous oxide.

Studies made at the Swedish Government Testing Institute showed that the folding endurance of paper and its copper number are closely related. When papers were subjected to a heat treatment, which was used as an accelerated aging test, those which had the highest copper number showed the greatest deterioration in folding endurance as a result of heating.[2] A limited number of tests made at the Bureau of Standards gave results which showed the same tendency. A number of samples of a particular commercial rag-fiber bond paper were tested and their folding values were found to be consistently in inverse proportion to their copper values. It appears that determination of copper number is of direct practical value and should be of service not only for testing the quality of paper, but as a part of the control procedure in the paper mill for maintaining satisfactory quality in the paper produced.

The method described below for the determination is patterned after the methods of Gault and Mukerji,[3] and Staud and Gray.[4] A stronger solution of potassium permanganate than that used by the first authors has been used in the following method: In the first method from 200 to 600 ml of potassium permanganate solution were required for a good quality paper, whereas in the following method a high-grade paper requires less than 10 ml. Gault and Mukerji obtained quite consistent results by a 15-minute treatment at the boiling temperature of the solution. Staud and Gray, on the other hand, have presented data to show that the reaction is not completed until nearly 30 minutes of treatment at this temperature, they, themselves, using 45 minutes as the reaction period. In the

[2] "Permanence of paper," Gösta Hall, Paper Trade J., **82**, No. 14; Apr. 8, 1926.
[3] Comp. rend., **178**, p. 711; 1924.
[4] Ind. and Eng. Chem., **17**, p. 741; 1925.

method described in this paper 30 minutes was found to give quite consistent results which did not vary greatly by longer treatment. Reduction of the test specimen to a finely divided condition is considered essential in reducing the time of treatment and producing complete reaction.

The method is particularly adapted to testing high-grade rag-fiber bond papers. Such papers are usually internally sized with rosin, surface sized with animal glue and pressed very hard in the finishing process. Owing to their hardness and toughness they are very resistant to the usual procedure employed for this determination but very accurate test results are obtained by the modifications described.

II. PREPARATION OF THE PAPER SAMPLE

In testing high-grade rag-fiber bond papers, because of the heavy glue surface sizing and the hard finish, it was found impossible to obtain accurate results which could be duplicated when a sheet of the paper was used or even if the paper were cut into very small fragments, although in the latter case much more uniform results were secured than in the former case. Uniform and accurate results were obtained only when the paper specimens were finely ground. The paper when ground had the appearance of finely cut cotton and was extremely well adapted to chemical treatment and washing. While such treatment may not be necessary in the case of soft, weak papers it is believed that grinding of the paper for this determination should be made standard procedure. In fact, such preparation of the paper is highly desirable for most chemical tests of paper which depend on extraction of the paper by liquid solvents, as paper fibers hold absorbed substances tenaciously.

The grinder used for this purpose was constructed similar to one used at the Swedish Government Testing Institute by Gösta Hall[5] and was designed by him. It consists of a 12-inch rotor fitted with six serrated steel lugs, which revolves inside a steel housing, the inner surface of which is also serrated around its circumference. The rotor teeth clear the stator teeth by a sixteenth of an inch. The rotor is driven at the rate of 1,700 revolutions per minute which gives the rotor teeth a speed of a little over a mile per minute. The dry paper is introduced in the form of strips through a slot and enters the rotor space near the center whence it is carried by centrifugal force into the space between the rotor teeth and the stator teeth. It is there disintegrated by impact and is ejected through a 7-mesh screen into a receiver in the base of the apparatus. Disintegration in this manner does not heat the paper, a consideration of much importance.

[5] "Acidity in paper," by S. Köhler, in charge of paper section, Government Testing Institute, Stockholm, Sweden, and G. Hall, chemist, Albemarle Paper Manufacturing Co., Richmond, Va.; The Paper Industry, 7, No. 7; October, 1925.

The advantage of using ground-paper samples instead of cut pieces is easily demonstrated by the molybdate method of titration. It is nearly impossible to remove all of the blue color of molybdenum from cut pieces, especially if the paper is heavily sized, whereas this washing process is accomplished with ease on the ground paper. The failure to remove all of the blue molybdenum in the washing process is a source of error which reduces the copper number. The blue color of the molybdenum is so intense as to afford a very good indication as to when the sample has been washed sufficiently, and for this reason is to be preferred to the iron solution commonly used.

III. PREPARATION OF THE SOLUTION

1. COPPER SULPHATE (FEHLING SOLUTION A)

To 4 liters of distilled water are added 277.3 g of copper sulphate ($CuSO_45H_2O$) and the mixture is shaken at intervals until the copper sulphate has gone into solution. The copper sulphate should be of high purity and as free from iron as possible.

2. ALKALINE TARTRATE (FEHLING SOLUTION B)

One hundred and fifty grams of sodium hydroxide of good quality and 500 g of sodium potassium tartrate are dissolved in 1,500 ml of distilled water.

3. FEHLING SOLUTION

Fehling solution is prepared by the careful addition of the copper sulphate solution (A) to an equal amount of the alkaline tartrate solution (B). It may be kept ready mixed, but should in this case be carefully protected from air and light, as it is apt to undergo changes which render its indications unreliable. Before using a mixed solution which has stood for some time, a small amount should be diluted and heated to boiling for a few minutes. A perfectly clear solution indicates that the solution is still satisfactory for use. It is, however, preferable to keep the two solutions separate until they are needed.

4. MOLYBDOPHOSPHORIC SOLUTION

Dissolve 100 g of sodium molybdate (43 per cent Mo) and 75 ml of phosphoric acid (83 per cent) in a solution containing 275 ml concentrated sulphuric acid and 1,750 ml of distilled water.

5. POTASSIUM PERMANGANATE SOLUTION

Dissolve 6.25 g of potassium permanganate in 1 liter of distilled water, filter through an asbestos mat in a Gooch crucible, and dilute to a total volume of 4 liters.

IV. STANDARDIZATION OF THE SOLUTION

The standardization is done according to the directions given in circular No. 40 of the Bureau of Standards,[6] with certain modifications due to the difference in the strength of the potassium permanganate solution. In a 400 ml beaker dissolve 1.5 to 2.0 g of sodium oxalate in 150 to 200 ml of hot water, 80° to 90° C., and add to this solution 6.5 ml of sulphuric acid (1 : 1). Titrate at once with the permanganate solution, stirring the liquid vigorously and continuously. The permanganate solution must be added slowly, not more than 10 to 15 ml per minute, and the last 0.5 to 1.0 ml must be added drop by drop with particular care to allow each drop to be fully decolorized before the next is added. The temperature of the solution at the end should not be below 60° C.

V. PROCEDURE

Determinations are always carried out in duplicate and if possible in triplicate, the final figure being an average of these separate values.

One and a half grams of the ground-paper sample are added to a solution of the following composition, after a temperature of 100° C. has been reached: 25 ml of copper sulphate solution, 25 ml of tartrate solution, and 125 ml of hot distilled water. This mixture is heated with gentle stirring in a 500 ml wide-mouth Erlenmeyer flask in a water bath containing 30 per cent calcium chloride. The temperature of this bath is maintained at about 110 to 115° C. so as to keep the liquid in the flask at a gentle boil during the time it is being treated. The temperature of the copper solution should not go below 100° C. during the period of treatment, which should be approximately 30 minutes.

The solution is then filtered while hot on a 5.5 cm filter paper[7] in a Büchner funnel and washed with 250 ml of hot water. The paper fiber and the filter paper are then transferred to a 250 ml beaker and 25 ml of the molybdate solution added. After allowing the mixture to stand for a short time 25 ml of water are added and the mixture stirred so as to disintegrate the filter paper. The solution is then filtered as before and washed with about 200 ml of cold water. This washing must be done thoroughly so as to remove all of the blue molybdenum color.

The blue solution is now titrated with the standard permanganate solution until a permanent pink is obtained. The titration can be carried out accurately without danger of adding an excess of permanganate since the blue solution changes to colorless just before it goes to pink and thus gives a definite warning of the approaching end point.

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[6] Government Printing Office, Washington, D. C., 5 cents each.

[7] A No. 40 Whatman filter paper gave good results.

VI. CALCULATION OF RESULTS

The copper number of the sample is determined by multiplying the number of milliliters of potassium permanganate used in the molybdenum titration by the calculated factor and dividing the result by the number of grams of sample used. The copper number may thus be defined as the number of centigrams of metallic copper in the cuprous oxide reduced from the cupric sulphate by 1 g of sample. The factor, which is dependent on the exact titer of the potassium permanganate solution, is the number of centigrams of copper, in the cuprous oxide, equivalent in reducing power to the oxidizing power of 1 ml of the potassium permanganate solution.

For example, the factor of a potassium permanganate solution is 0.2714; that is, 1 ml $KMnO_4 = 0.2714$ cg Cu. In an analysis, using 1.5 g of sample, 5 ml of potassium permanganate solution are required in the titration. The copper number of the sample is calculated as follows:

$$\frac{\text{ml}KMnO_4 \times \text{factor}}{\text{Grams of sample}} = \frac{5.0 \times 0.2714}{1.5} = 0.9046$$

or the copper number of the sample.

Washington, June 18, 1927.